Oxygenated and Nitrated Polyaromatic Hydrocarbons in Ambient Air: Levels in Gas-Particulate Phase, Source Identification and Risk Assessment

SYNOPSIS

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SIMRAN BAMOLA

UNDER THE SUPERVISION OF

PROF. ANITA LAKHANI

DEPARTMENT OF CHEMISTRY, FACULTY OF SCIENCE

DAYALBAGH EDUCATIONAL INSTITUTE (TO BE DEEMED UNIVERSITY)

DAYALBAGH, AGRA-282005

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1. INTRODUCTION

Air pollution continues to present one of the world's biggest health hazards to people everywhere, contributing to about 7 million premature deaths annually (HEI, 2020). According to world air quality report, 2021 India ranks at fifth position globally (annual average $PM_{2.5}$ = 58.1 μg/m^3 in 2021), experiencing the worst air quality with 48% of cities with $PM_{2.5}$ concentrations greater than ten times the WHO, 2021 air quality guideline level (5 μg/m^3) (IQAir, 2020). According to epidemiological and toxicological studies particulate matter (PM) has been related to the chronic consequences of air pollution such as health problems and climate alteration concerning meteorological parameters (Charrier and Anastasio, 2015), (Charrier et al., 2014). Recent studies are more focused on the PM, due to its complex nature, variety of chemical distributions, concentration, compositions and most importantly its microscopic size (<10μm in diameter) that can penetrate deeper into the human respiratory system (Cervellati et al., 2020). These PM consists of primary particles, which are emitted directly to the atmosphere as a result of incomplete combustion processes or are produced by the abrasion of tires, or brakes, road surfaces, and by the generation of fugitive dust. Additionally, PM also comprises secondary particles, which are generated chemically from gaseous precursors in the atmosphere. The basic composition of these particles includes inorganic (salts, metals, elementary carbon), organic compounds [alkanes, alcohols, fatty acids, volatile organic compounds (VOCs), Black Carbon, Polyaromatic Hydrocarbons (PAHs) and their derivatives like NPAHs, OPAHs and quinones] and transition metals. Many researchers have identified these components of PM responsible for generation of large number of health impacts involving asthma, allergies, skin cancer, cardiovascular pulmonary diseases (COPDs) etc. (Hamanaka and Mutlu, 2018); (Wu et al., 2018).

PAHs are a class of potentially carcinogenic, mutagenic and ubiquitous semi-volatile aromatic organic pollutants detected in numerous environmental media and geographic regions (Abdel-Shafy and Mansour, 2016). They consist of conjugate π–π bonds, which also provide them stability and longer lifetime in the environment. They are produced mainly through incomplete combustion or pyrolysis of organic materials. Major anthropogenic sources include coal and wood burning, petrol and diesel oil combustion and industrial emissions (Hamanaka and Mutlu, 2018), (Wu et al., 2018) whereas volcanic eruptions and biomass burning are the natural sources. They can exist in several isomeric forms and

structures due to the presence of more than two benzene rings (having conjugated π–π bonds). They are resistant to degradation and therefore are classed as persistent organic pollutants (POP's) by the Convention on Long-range Transboundary Air Pollution. The PM are considered to be most efficient and prominent surface for the adsorption of PAHs in air. In particular, fine particles, carrying PAHs, can adversely affect human by penetrating and depositing deeper into the lungs. Over 95% of PAHs are bonded on particles with a size fraction of less than 3 μm which can easily enter into the human respiratory tract (Wei et al., 2010). Therefore, making PAHs a prominent topic of research in both toxicological and atmospheric chemistry (Pietrogrande et al., 2023).

PAHs are partitioned between the vapour and particulate phase in the atmosphere due to their semi volatile nature. The vapour phase contains pre-dominantly the low molecular weight (LMW) PAHs [naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Fluo), phenanthrene (Phen), and anthracene (Anth)] with a molecular weight ranging from 128-178 Da comprising two to three fused benzene rings and medium molecular weight (MMW) PAHs [pyrene (Pyr), benzo(a)anthracene (BaA), and chrysene (Chry)] containing 4-ring PAHs having molecular weight ranging from 202-228 Da whereas high molecular weight (HMW) PAHs [benzo(b)fluoranthene(BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz(a,h)anthracene (DbA), indeno(1,2,3-cd)pyrene (IP) and benzo[g.h.j]perylene (BghiP)] with five or more fused rings having molecular weight ranging from 252 – 278 Da are mainly associated with particulate phase of matter. The partitioning of PAHs depends mainly on the physico-chemical properties of individual PAH, size distribution, concentrations of organic and elemental carbon (OC and EC), total suspended particle (TSP) concentration and meteorological parameters like ambient air temperature and relative humidity (Verma et al., 2021). The concentration of each PAH in these phases is determined by its volatility and affinity to the surface of atmospheric particles. Also, their atmospheric occurrence, transformations, dry deposition, wet deposition, concentration in the atmosphere, reactivity (lifetime and persistence), routes of entering the human body and bioavailability all depends on the gas-particle partitioning (Verma et al., 2017).

The-gas phase PAHs possess higher tendency to interact with other atmospheric pollutants like ozone (O_3), nitrogen oxides (NO_x), hydroxy (OH) to form derivatives of PAHs in the atmosphere such as Nitro-, Oxy-, Hydroxy- and Chloro-PAHs (Alam et al., 2013). These derivative compounds mainly

oxy-PAHs (OPAHs) and nitro-PAHs (NPAHs) are $2x10^5$ times more mutagenic and 10 times more carcinogenic than their parent compounds (Lakhani, 2018). Like PAHs, a small fraction of these derivatives is also emitted from primary sources like automotive emissions, industrial emissions while a larger fraction is formed by secondary transformations, heterogenous and homogenous reactions, thermal and photolytic degradation of parent PAHs. These compounds in atmosphere are light sensitive and exposure to UV radiation damages their form and structure. In comparison to particle-bound HMW-PAHs, the LMW-PAHs are more vulnerable to direct or indirect photodegradation. Their superior chemical stability and proclivity to adsorb onto the surface of PM or carbonaceous materials makes HMW-PAHs more photo-resistant than LMW-PAHs. Their persistence and high toxicity, makes them responsible for a wide range of health impacts that are proportional to their concentration, exposure route, exposure rate, and exposure duration. As PAHs are abundant in both the gas and particle phases of the environment, they can easily enter the human body via ingestion, inhalation, and skin exposure.

PAHs and their derivatives pose the most significant health threats due to their propensity to stimulate the formation of reactive oxygen species (ROS), which operate as mediators of cardiovascular effects, increasing the risk of cancer in humans. The carcinogenic action of PAHs is dictated by their metabolic activation into electrophiles, catalysed by different enzymes via free radical processes.

These metabolic activation pathways include:

(a) generation of diol epoxides, catalysed by several cytochrome P_{450}, leading to DNA adduct formation which are considered essential to PAH carcinogenesis.

(b) formation of radical cations, catalysed by P_{450} peroxidases, (CYP_{450}), epoxide hydrolases, Aldo keto reductases that results in formation of highly toxic metabolites viz. 1,4-benzoquinone, naphthoquinone, phenanthroquinone, anthraquinone, etc.

(c) formation of redox active o-quinones, catalysed by dihydrodiol dehydrogenases, which can contribute to PAH carcinogenesis by acting as tumour promoters (Valavanidis et al., 2011).

(d) UV light activation of PAHs to form toxic derivatives producing ROS and reactive intermediates that can damage DNA, protein and cell membrane, resulting in acute toxicity, genotoxicity and skin cancer (Yu et al., 2006).

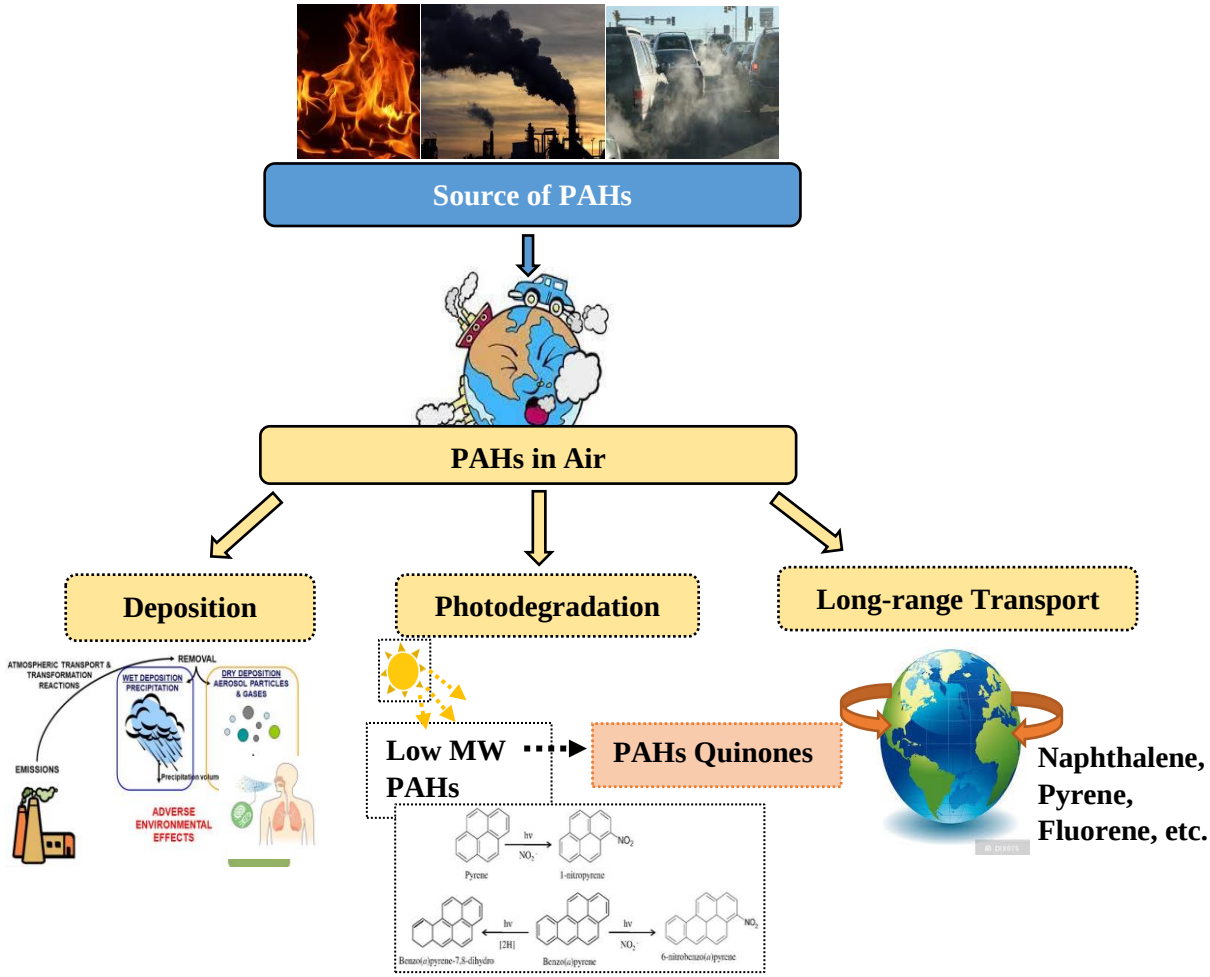

Fig-1 *Fate of PAHs in air*

PAHs in air can undergo various processes such as deposition, photodegradation and long-range transportation as shown in Fig-1. Despite the fact that there are a large number of PAHs in the environment, only 16 of them are on the United States-Environmental Protection Agency's (US-EPA) priority list of PAHs [Nap, Ace, Acy, Fluo, Phen, Anth, Fla, Pyr, BaA, Chy, BbF, BkF, BaP, IP, DbA, BghiP]. Recent air monitoring has revealed that the yearly average concentrations of respirable suspended particulate matter (RSPM) and suspended particulate matter (SPM) in most Indian cities surpassed the National Ambient Air Quality Standards (NAAQS) guidelines. The prevalence of PAHs and their complex mixture of structural isomers and derivatives in the environment, as well as their associated carcinogenic effects, has prompted international regulations, such as those under the United Nations Economic Commission for Europe's Convention on Long-Range Transboundary Air Pollution. Furthermore, the Environmental Protection Agency of the United States, the International

Agency for Research on Cancer, and the National Toxicology Program have classed several PAH compounds as extremely carcinogenic and mutagenic in nature. National Ambient Air Quality Standards (NAAQS) limits (100 g/m^3 for RSPM; 200 g/m^3 for SPM; India) (CPCB, India 2009). Thus, presence of these carcinogenic PAHs in respirable particulate fractions (<10 μM size), poses a serious threat to human health and demands its regular monitoring (Gurbani et al., 2013).

Over the last decade increasing attention has been given to PAH derivatives i.e., NPAHs and OPAHs because of their increased degree of mutagenicity, carcinogenicity (Clergé et al., 2019). NPAHs and OPAHs are co-emitted with soot in all combustion processes and are prevalent in polluted air. Several NPAHs and OPAHs are produced by PAH photoreactions and are found to generate reactive oxygen species in greater proclivity than parent PAHs, conferring greater toxicity (Lammel et al., 2020). Though research on NPAH estimation, concentration, and consequences in the environment are widely documented, there is relatively limited number of studies on OPAHs globally while no research has been performed nationally i.e., in India. OPAHs have been postulated to be "dead-end products" of PAHs because of their high oxidation state, leaving the toxicity of these molecules largely unknown (Clergé et al., 2019).

Recently, PAH quinone derivatives have piqued the interest of researchers due to their role in increasing oxidative stress levels (Barradas-Gimate et al., 2017). These derivatives, can easily adsorb on the surface of particulate matter and penetrate deep into the human respiratory system, where on deposition and adsorption they undergo a number of chemical transformation pathways including direct DNA, lipid or protein binding, and redox cycling, which elicit changes in the redox status of cells through their ability to carry out electron transfer reactions, resulting in the generation of ROS. They also establish covalent connections with tissue macromolecules, resulting in inactive cellular proteins, eventually leading to mutations and cancer as depicted in Fig. 2 (Gurbani et al., 2013). Due to the increased ability of PAHs,

OPAHs, and NPAHs to generate ROS, they are classified as highly toxic species in the atmosphere.

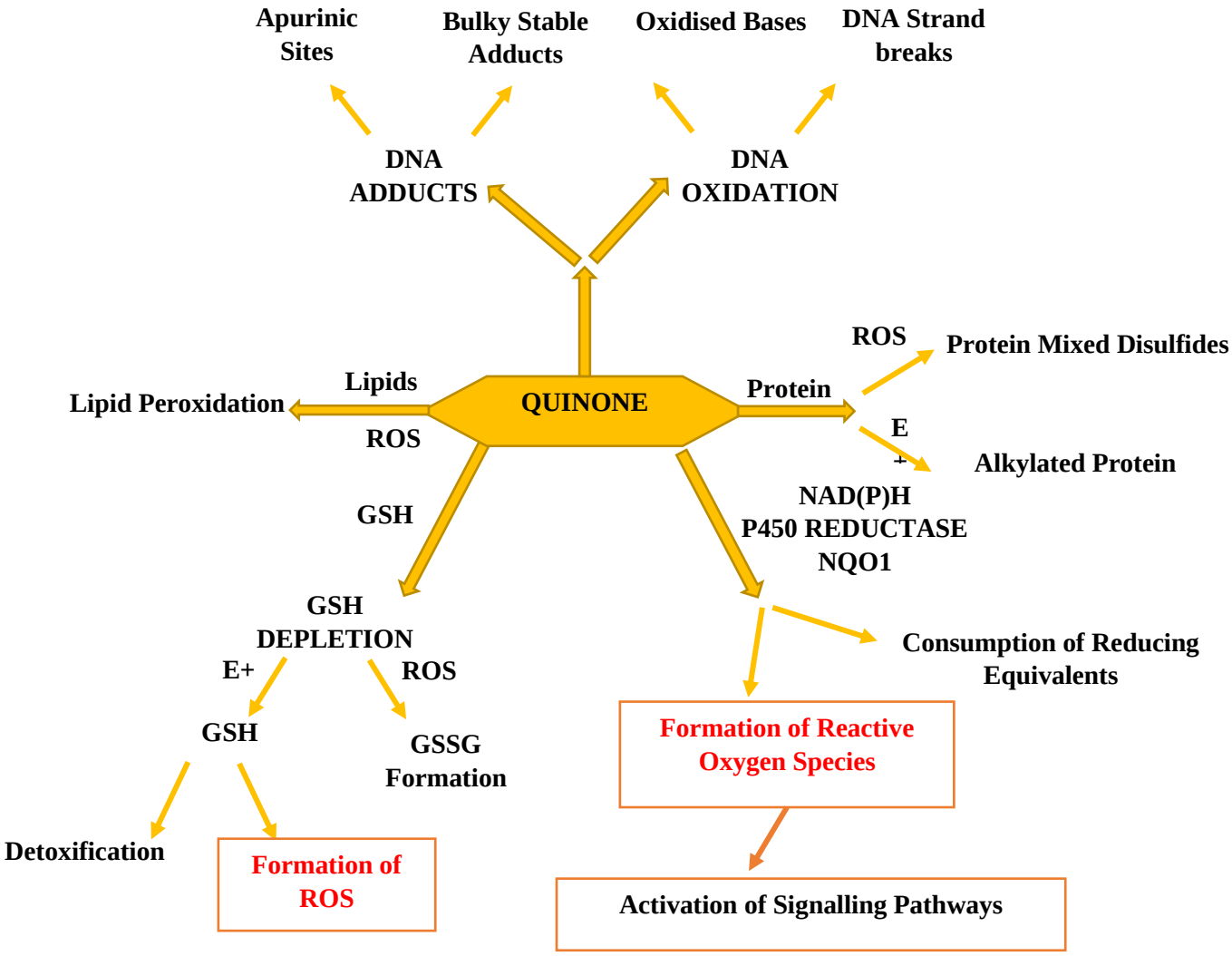

Fig-2 *Potential cytotoxicity mechanism of quinones*

During redox cycling, reduced quinoid converts oxygen (O_2) to generate superoxide radicals, which then give rise to the hydroxyl radical as shown in Fig-3. This $^{\bullet}OH$ is the most damaging of the ROS, reacting with most biological molecules, including DNA, at diffusion-controlled rates. Semiquinone radical anion species are the catalytic intermediates in redox cycling mechanism. Thus, quinones operate as a good oxidant in redox cycling, accepting an electron from biological reductants [Ascorbic acid, Catechol, Dithiothreitol (DTT)] (Charrier et al., 2014), whereas the equivalent semiquinone species act as a good reductant, rapidly

reducing O_2. As with ozone (O_3), ROS induce oxidative damage by oxidising biological molecules and/or activating the release of proinflammatory mediators. Biological reducing equivalents [e.g., ascorbate, nicotinamide adenine dinucleotide phosphate NAD(P)H, glutathione, etc.] return oxidised quinoid compounds to their reduced forms, allowing them to create the superoxide radical ($O_2^{-\cdot}$) once again. In the presence of Fe, this quinone-mediated H_2O_2 synthesis accelerates the Fenton reaction and increases •OH generation (Charrier et al., 2014). This process is repeated several times. It is crucial to note that the redox cycling mechanism that creates superoxide under these conditions is stoichiometric in reducing equivalents but catalytic in quinoid substances. Increased superoxide radical production promotes the interaction of superoxide radicals ($O_2^{-\cdot}$) with cellular nitric oxide (NO), resulting in the generation of peroxynitrite ($ONOO^-$) and other reactive species.

Quinone redox cycling can therefore result in lipid peroxidation, decreasing equivalent consumption, DNA oxidation, and DNA strand breakage as shown in Fig-4. Additionally, the mutagenicity and carcinogenicity of several quinones is explained by their proclivity to create DNA adducts. All of these OPAH characteristics have a negative impact on pulmonary cells, attracting human concern (Eiguren-Fernandez et al., 2008).

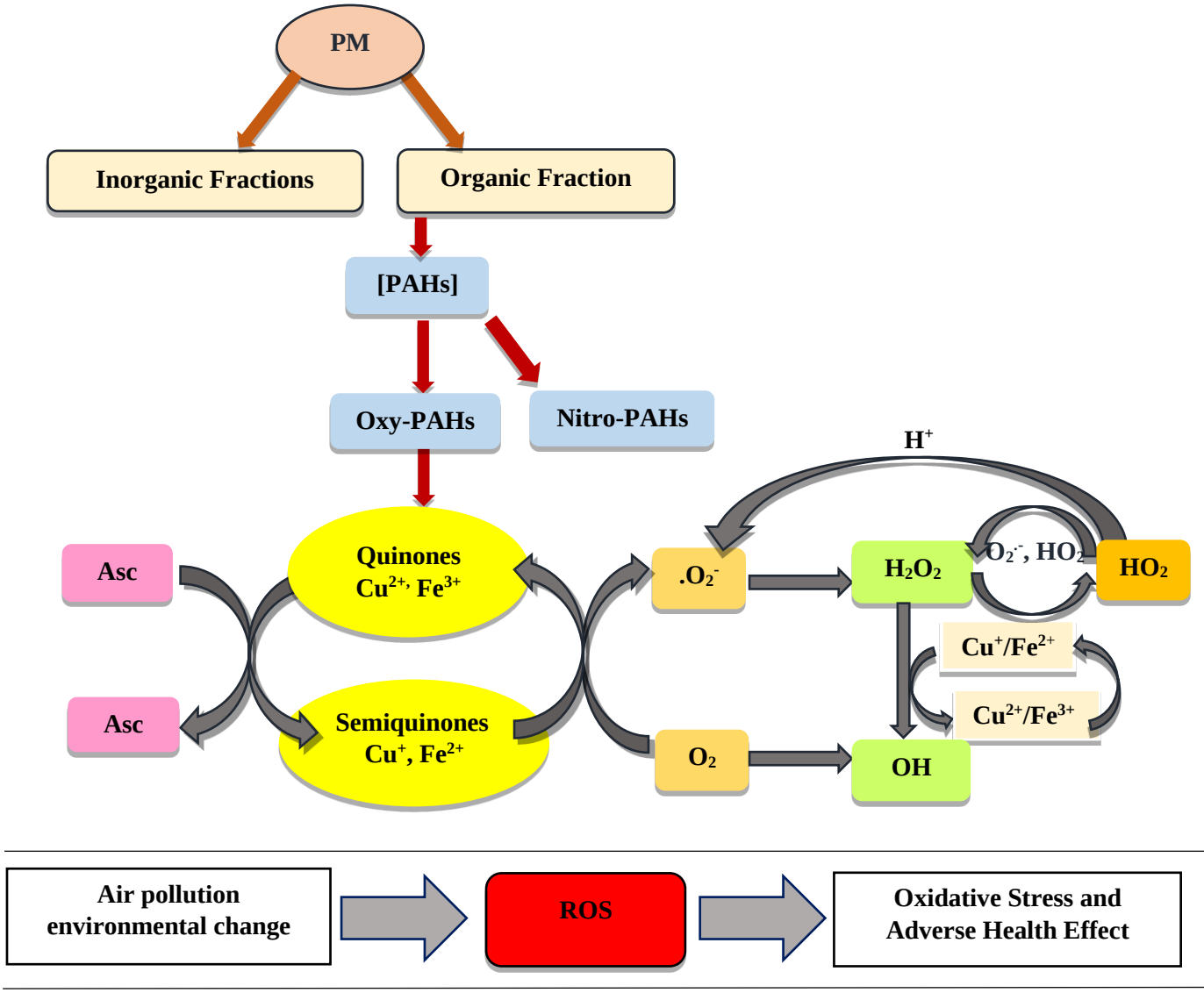

Fig 3*- Mechanism of ROS generation from Quinone redox cycling*

$QH_2 + Q$	--->	$2Q^{\bullet -} + 2H^+$	R_1
$Q^{\bullet -} + O_2$	--->	$Q + O_2^{\bullet -}$	R_2
$QH_2 + O_2^{\bullet -}$	--->	$QH^{\bullet -} + HO^{2\bullet}$	R_3
$QH^{\bullet -} + HO^{2\bullet}$	--->	$Q^{\bullet -} + H_2O_2$	R_4
$O^{2\bullet -} + O^{2\bullet -} + 2H+$	--->	$H_2O_2 + O_2$	R_5

[Hydroquinone undergoes auto oxidation with a quinone (Q) to form a semiquinone ($Q^{\bullet -}$) intermediate (R_1). The semiquinone intermediate reduces molecular oxygen to generate superoxide radical anion $O_2^{\bullet -}$ (R_2). Spontaneous deprotonation of QH_2 takes place when QH_2

interacts with superoxide radical anion $O_2^{\bullet -}$ (R_3). The $QH^{\bullet -}$ formed is oxidized to generate the semiquinone radical and hydrogen peroxide (R_4). Superoxide radical anions generated in R_2 can react with another $O_2^{\bullet -}$ and two hydrogen ions to generate hydrogen peroxide (R_5).]

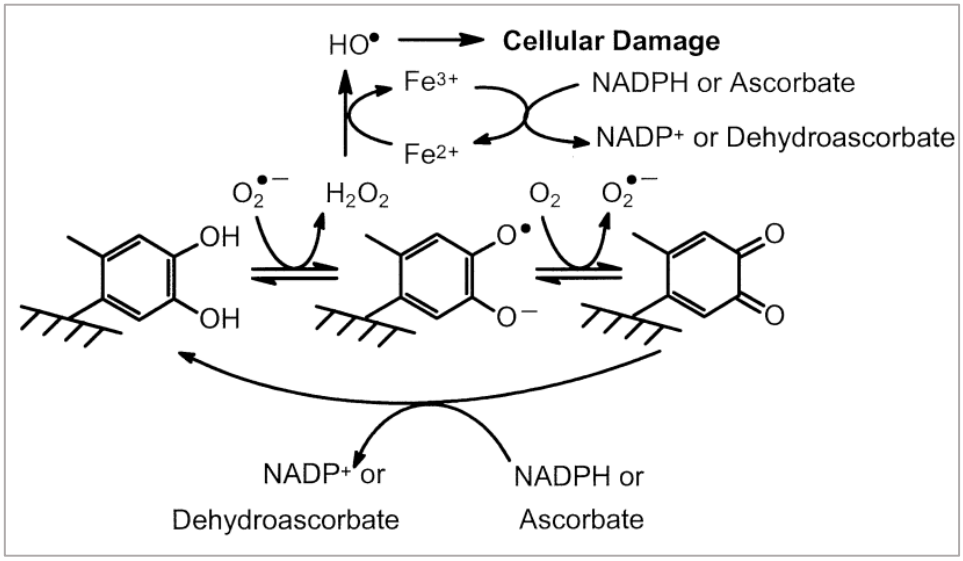

Fig-4 *Quinone redox cycling* (Squadrito et al., 2001)

Quinones have long been recognised as very effective DTT oxidation catalysts; nevertheless, their exact contribution to ambient PM DTT activity is debatable. Most investigations found that primary quinones contribute very little (20%) to the water soluble DTT activity of ambient PM, with oxygenated derivatives likely contributing more (hydroxyquinones). Several quinones have been found in ambient particles, but only 1,2-NQ, 1,4-NQ, and 9,10-PQ have found to contribute to DTT action at atmospherically relevant quantities (Squadrito et al., 2001).

Although parent PAHs have been routinely monitored in ambient air, only a few studies have reported ambient quinone concentrations. As the amounts of quinones found in PM are very small, compared with other toxic and carcinogenic compounds (e.g., PAHs, NPAHs, metals), their function in redox cycling mechanisms and their involvement in the formation of ROS and oxidative damage to biomolecules make them interesting air pollutants in terms of

cytotoxicity. Today the toxicology of quinones has been well documented, but extensive studies related with measurements of their atmospheric levels, phase distribution, and the adverse health effects associated with exposure to these compounds have not been performed (Eiguren-Fernandez et al., 2008).

2. LITERATURE REVIEW-

International Status

Globally PAHs and their derivatives (OPAHs and NPAHs) in the atmosphere have been rigorously investigated and found highly carcinogenic and mutagenic in nature for human beings (Delgado-Saborit et al., 2013), (Bandowe et al., 2014), (Walgraeve et al., 2015). However, the PAHs concentrations in ambient air are generally one to two orders of magnitude higher than those of OPAHs, NPAHs (Wei et al., 2021). A number of studies identified their concentration in various parts of the world at different rural, urban, sub-urban sites as mentioned in Table 1 (Li et al., 2015), (Tomaz et al., 2016), (Lammel et al., 2020). PAHs are semi-volatile in nature thus can be present in atmosphere in both gaseous and particulate phase. Studies conducted by Zhang et al., 2018, Li et al., 2016, Wei et al., 2015 have identified and quantified PAHs and its derivatives in both the gas and particulate phase in different environments all over the world and also identified numerous factors, such as emission source, particle properties and meteorological conditions, that influence the gas-to-particle partitioning of polycyclic aromatic compounds (PACs). PAH are identified in air samples direct emission of several sources such as domestic combustion, natural gas combustion in residential appliances, tobacco smoke (Ding et al., 2011) and gasoline and diesel vehicle exhaust (Yang et al., 2010). Due to their high reactivity and reactions with atmospheric oxidants like O_3, NO_2, OH their derivative compounds were investigated for their potent toxicity.

Many studies quantified variety of NPAHs and OPAHs in the ambient air particulate samples collected at various sites of different countries like Central Los Angeles, Southern California (Cho et al., 2004), Perkin University, Beijing China (Wei et al., 2010), traffic site in

Guangzhou (Gao et al., 2011), urban settings and rural villages in Northern China (Li et al., 2015), urban and regional background sites in central Europe (Lammel et al., 2020) which is also mentioned in Table 2 and 3. Few of the studies also identified their partitioning mechanism and determined their concentration in gaseous and particulate phase where the lower molecular weight PAHs were identified in gaseous phase and higher molecular weight PAHs into particulate phase (Tomaz et al., 2016), (Wnorowski and Charland, 2017), (Lammel et al., 2020). Several studies were conducted to identify the concentration of PAHs and derivatives in various size fraction of PM such as $PM_{2.5}$ (Gao et al., 2011), (Nocun and Schantz, 2013), (Sousa et al., 2015), PM_{10} (Walgraeve et al., 2015), (Ju et al., 2020). A range of standard samples like SRM 1649a, Diesel Exhaust Particle (DEP) SRMs (1649b, 1648a, and 2786) and diesel PM SRMs (1650b, 2975, and 1975) (Cho et al., 2004), (Nocun and Schantz, 2013) were further used for the detection and comparison of these derivatives compounds in the atmosphere.

Recently, the role of oxy-PAHs in causing oxidative stress has found great attention and few researchers assessed their variation in different seasons at China (Lee et al., 2018), South Korea (Ju et al., 2020), Europe (Lammel et al., 2020) and found higher concentration in winters than in summer suggesting dominant influence of emissions from household heating and winter meteorological conditions. A lot of researchers have quantified and identified these PAHs and its derivatives using GC-MS (Gas Chromatograph - Mass Spectrometry) few others have used other analytical techniques like High Performance Liquid Chromatography (HPLC), Programmed temperature vaporization injection (PTV) gas chromatography coupled with high resolution mass spectrometry (Walgraeve et al., 2015)for the detection of OPAHs and NPAHs. (Wei et al., 2010) examined 24 PAHs and anthraquinone (AnQ) in $PM_{2.5}$ and related it with oxidative stress in human exposed to heavy traffic volume at Perkin University, Beijing China. Likewise, Charrier et al., 2014 showed the activity of OPAHs in oxidising DTT and producing reactive oxygen species by 20% along with water soluble transition metal which contributes

about 80% of the PM fraction. Ju and Ki, 2021 showed results to justify the correlation between ROS generation from ambient air PAHs by showing its effect on vascular smooth muscle cell (VSMC). Sousa et al., 2015 identified quinones in both the nonderivatized and acetylated derivatised forms and found good correlation of analysis of quinone in nonderivatized form. Study by Barradas-Gimate et al., 2017 added to the influence of meteorological factors like solar radiation and relative humidity into the formation of OPAHs mainly Quinone into the ambient atmosphere of Guadalajara, Mexico. Due to the importance of the PAC in ambient air, different studies have been carried out to quantify PAHs in air samples around the world: Spain (Bernalte et al., 2012); Serbia (Vuković et al., 2014); Japan (Yagishita et al., 2015); Portugal (Albuquerque et al., 2016); China (Ren et al., 2017); USA (Liu et al., 2017); Iran (Jaafari et al., 2020).

Table 1. International Status of PAHs Estimation

Sampling Site		Site Type	Duration	Sampling Type	No. of PAHs	Concentrations of PAHs (ng/m^3)	References
Spain	Ciudad Real	Urban	Nov, 2017-Oct, 2018	PM_{10}	7	0.13-5.65	Lara et al., 2022
Norway	Longyear byen	Urban	Nov, 2017-June, 2018	Gas + PM	22	1068 ± 449 pg/m^3	Drotikova et al., 2021
Brazil	Belo Horizonte	Urban	One Year	$PM_{2.5}$ + Gas	16	0.49	Santos et al., 2020
Iran	Tehran	Urban	22, Dec, 2016 – 5, June, 2017	PM_{10}	16	103.8-28.1	Jaafari et al., 2020
		Rural				31.85-15.72	
China	6 Cities (Xian, Sichuan, Hubei, Guangdong, Beijing, Zhang)	Urban	2 weeks (23, Nov – 6 Dec, 2019)	$PM_{2.5}$	22	19.42-65-40	Sun et al., 2022
	Beijing	Urban	22, Nov – 9, Dec, 2016	$PM_{2.5}$	16	37-180	Elzein et al., 2019
	Jinan	Urban	Dec, 2014 to Jan,2015	TSP + Gas	18	305.91	Zhang et.al., 2018

	Mount Tai	Mountain	16-21 Nov,2014			37.83	
	Mount Heng	Mountain Site	Mar-May,2009	TSP + Gas	15	24.1	Li et.al., 2016
	Xian	Urban	Mar,2012	TSP + Gas	29	1267.0 ± 307.5	Wei et.al., 2015
		Industrial	Sep,2012	TSP + Gas	-	728.6 ± 131.9	
		Commercial and Traffic				40.2 ± 33.3	
	Gubiekou	Rural	Sep,2007-Aug,2008 Apr,2005-Mar,2006	TSP + Gas TSP + Gas	- 16	242.4 ± 244.4	Yang et al., 2010
	Donghe	Rural				730.7 ± 608.0	
	Beijing	Urban				405.8 ± 398.7	
	Guangzhou	Urban				120.4	
Mexico	Guadalajara	Urban	2014	$PM_{2.5}$	16	0.03-0.82	Barradas-Gimate et al., 2017
Japan	Osaka	Urban	2005-2006	TSP + Gas	28	59.88	Kishida et al., 2011
France	Grenoble	Summer Winter One year	-	Gas + PM_{10}	21	41.7 24.5	Tomaz et al., 2016
	Marchseille	Urban Sub-Urban Rural	-	Gas + PM_{10}	15	21.4	Delgado-Saborit et al., 2013
UK	Marchseille Birmingham	Rural	- -	Gas + PM_{10} -	15	4.4	Cincinelli et al., 2007
		Sub-Urban				16	
		Urban				87.6	
Turkey	Zonguldak	Industrial	May,2007-Apr,2008	TSP + Gas	16	114 - 184	Akyüz and Çabuk, 2010
	Bursa	Urban	-	TSP + Gas	-	230.9	Vardar et al., 2008
Egypt	Giza, Dokki	Urban	2007-2008	TSP + Gas	15	4342	Hassan and Khoder, 2012
USA	MBO	-	Apr,2004-May,2006	TSP + Gas	14	<6	Primbs et al., 2008

Table 2. International Status of NPAHs Estimations

Sampling Site		Site Type	Duration	Sampling Type	No. of NPAHs	Concentrations of NPAHs (ng/m^3)	References
China	Guangzhou	Urban Sub-Urban	2019-2020	$PM_{2.5}$ + TSP	3	0.085-0.116 in $PM_{2.5}$ 0.797-1.11 in TSP	Gao et al., 2022
	Jinan	Urban	Dec,2014-Jan,2015	Gas + TSP	18	24.8	Zhang et al., 2018

	Mt. Tai.	Mountain	16-21, Nov,2014			0.27	
	Xi'an	Urban	2008-2009	$PM_{2.5}$	12	0.3-7	Bandowe et al., 2014
	Qingyuan	-	2009-2010	$PM_{2.5}$	13	0.04-0.7	Wei et al., 2012
	Beijing	Urban	2008	$PM_{2.5}$	11	0.07-3	Wang et al., 2011
Spain	Ciudad Real	Urban	Nov, 2017-Oct, 2018	PM_{10}	7	0.30	Lara et. al., 2022
	Barcelona	Urban	One year	PM_{10}	5	0.12	Barrado et al., 2013
	Madrid	Urban	2008-2009	PM_{10}	5	0.11	
Europe	Central Europe (Brno, Ljubljana Czech Republic)	Urban and Rural	2017	$PM_{2.5}$	9	593 pg/m^3	Degrendele et al., 2021
	Central Europe	Urban	2016-2017	PM_{10} + Gas	18	0.09−8.1	Lammel et al., 2020
		Rural Background Site				0.004−0.14	
Brazil	Belo Horizonte	Urban	One Year	$PM_{2.5}$ + Gas	16	0.49	Santos et al., 2020
France	Paris	Urban	2009 -2010	PM_{10}	19	0.03 -0.18	Ringuet et al., 2012
	Grenoble	Urban	Jan, 2013-Jan, 2014 All Year	Gas + TSP	32	0.07	Tomaz et al., 2016
Portugal	Oporto	Traffic	Jan,2013-Feb,2014	$PM_{2.5}$	15	15.8-9.15	Alves et al., 2017
Italy	Florence	Background				10.9-3.36	
Greece	Athens	Sub-urban				15.9-2.73	
USA	Baltimore	Urban	Winter	Gas + PM_{10}	26	0.31	Bamford and Baker, 2003
		Sub-Urban	Summer			0.25	
	Fort Beade	Urban	Winter			0.19	
		Sub-Urban	Summer			0.06	
Mexico	Mexico City	Urban	Year	$PM_{2.5}$	9	0.12	Amador-Muñoz et al., 2011
	Mexico Valley	Sub-Urban	2006	$PM_{2.5}$	9	0.11-0.12	

Table 3. International Status of $OPAH_S$ Estimation

Sampling Site		Site Type	Time Duration	Sampling Type	No of OPAHs	Concentrations of OPAHs (ng/m^3)	References
Spain	Ciudad Real	Urban	Nov, 2017-Oct, 2018	PM_{10}	7	0.05-2.06	Lara et. al., 2022
China	6 Cities	Urban	2 weeks	$PM_{2.5}$	10	19.42-65-40	Sun et.al., 2022

			(23, Nov – 6 Dec, 2019)				
	Beijing	Urban	22, Nov – 9, Dec, 2016	$PM_{2.5}$	10	13-70	Elzein et.al., 2019
Europe	Central Europe	Urban	2017	$PM_{2.5}$	11	1.64-4330 pg/m^3	Degrendele et al., 2021
Norway	Longyear byen	Urban	Nov, 2017-June, 2018	Gas + PM	29	5934 ± 1480 pg/m^3	Drotikova et.al., 2021
Brazil	Belo Horizonte	Urban	One Year	$PM_{2.5}$ + Gas	6	0.49	Santos et.al., 2020
Europe	Central Europe	Urban	2016-2017	PM_{10} + Gas	10	2.3−34.2	Lammel et.al., 2020
		Rural Background Site				0.26−9.0	
South Korea	Seoul	Urban	Sep,2006-Aug,2007	PM_{10}	7	1.47-8.7	Lee et al., 2018b
Mexico	Guadalajara	Urban	2014	$PM_{2.5}$	7	0.15-0.42	Barradas-Gimate et.al., 2017

National Status

It is also alarming to note that annual PAH emissions from Asian countries were 290 Gg/year, with China and India contributing 114 and 90 Gg/year, respectively. The proportion of high molecular weight PAH emission from India (3.60%) was significantly higher than the global average. A large amount of data on concentration levels of particulate matter, NOx, SO_2, and CO are available for prominent urban areas in India, studies on measurements of PAHs in the ambient air of major cities are rather limited. The studies so far conducted are on PAH composition in only the respirable suspended particulate phase (Ambade et al.,2021)**;** (Gope et al., 2020); (Kumar et al., 2020); (Masto et al., 2019a)**;** (Mitra et al., 2019)**;** (Mohanraj et al., 2011a); (Singh et al., 2016); (Tarafdar and Sinha 2019)**;** (Tiwari et al., 2020) and gas-phase PAHs have been rather very few in number (Verma et al., 2017) as mentioned in Table 4. Studies discussing the G-P partition of PAHs and levels of NPAHs however has been reported but that are also very low in number. Thus, this PAHs determination specially its derivatives demand great attention and need for research. Also, no single study has taken OPAH into account despite of its large toxicity for identification and quantification purpose in the

atmosphere. In India PAH concentrations have been monitored at various locations to evaluate the carcinogenic risk from PAH exposure, such as Punjab (Kaur et al., 2022)**,** (Kumar et al., 2014), Dhanbad (Tarafdar and Sinha, 2019), (Masto et al., 2019b), Mumbai (Tiwari et al., 2020), Jharkhand (Kumar et al., 2020), Calcutta (Gope et al., 2020)**,** (Saha et al., 2017)), Lucknow (Ansari et al., 2010); (Pandey et al., 2013); (Singh et al., 2016), Delhi ((Singh et al., 2021)**,** (Hazarika et al., 2017), (Gadi et al., 2012); (Gurbani et al., 2013)**;** (Mandal, 2012)**;** (Sarkar and Khillare, 2011), Chennai (Mohanraj et.al., 2011a), Tiruchirappalli (Mohanraj et al., 2011b), Agra (Lakhani, 2018), (Masih et al., 2010)**,** (Masih et al., 2012), Tamil Nadu (Sampath et al., 2015). PAHs were also investigated into various size fraction of PM like $PM_{2.5}$ and PM_{10} at different locations and sites in India (Ansari et al., 2010); (Masih et al., 2010); (Mohanraj et al., 2011a); (Mohanraj et al., 2011b); (Mandal, 2012); (Hazarika et al., 2017); (Tiwari et al., 2020); (Ambade et al., 2021); (Kaur et al., 2022). Based on available literature PAHs concentration at various sites across Indian cities are shown in Table 4.

Table 4. National status of PAH & NPAHs estimation

Location	Site Type	Time Period	Sampling Type	Number of PAHs	Concentrations of PAHs (ng/m^3)	References
Punjab	Urban	Nov, 2013-Jan, 2014	PM_{10}	16	18-164	Kaur et al., 2022
Jharkhand	Ranchi, Gamharia, Bokaro	June,2018-June, 2019	$PM_{2.5}$	16	887.7 ± 38.8 1015.1 ± 42.7 797.9 ± 39.1	Ambade et. al., 2022
	Jamshedpur Semi-Urban, Rural, Urban	Dec, 2016 – May, 2017	$PM_{2.5}$	16	-	Kumar et. al., 2020a
	Urban,	Jan – Dec, 2018	$PM_{2.5}$	16	750.80 ± 19.49	Kumar et al., 2020b
	Rural				559.59 ± 17.56	
Mumbai	Urban	Mar - May, 2018	Size Segregated PM	15	101- 145	Tiwari et al., 2020
	Urban	2007-2008	PM_{10}	8	48	Harlekar et. al., 2012
Delhi	5 sites (Mukherjee	One Year	Gas + $PM_{2.5}$	16	30.04 – 222.94 in $PM_{2.5}$,	Singh et. al., 2021

	Nagar, Anand Vihar, Rohini, CP, JNU)				30.16- 80.16 in Gas	
	Urban, Industrial	2008-2009	PM_{10}	16	83	Sarkar and Khillare, 2011
	Urban, Residential				102	
	Urban Residential, Industrial				130	
West Bengal	Durgapur Rural	2013- 2014	$PM_{0.1}$-$PM_{21.3}$	16	2317 ± 402 to 5491 ± 2379	Gope et. al., 2020
	Kolkatta Urban	2015-2016	PM_{10}	14	88.4	Ray et.al., 2017
Jamshedpur	Urban	Dec, 2016 – May, 2017	$PM_{2.5}$	16	190.2	Kumar et. al., 2020
	Semi-Urban				87.34	
	Rural				73.33	
Karnataka	Urban	2009 – 2011	Soil + Gas	16	0.71 – 2.99 in air, 1.59 – 22.7 ng/g in soil	Gune et al., 2019
Dhanbad	Urban	27, Aug 2012 to 31, Aug, 2012	Road Dust PM_{10}, $PM_{2.5}$	16	3.98-13.1 mg/g, 0.018-0.133 in PM_{10}, 1.08 in $PM_{2.5}$	Mastro et al., 2019
	Urban	Oct-Dec, 2016	Soil	13	8.256-12.562 µg/g	Tarafdar et. al., 2018
Darjeeling	Urban, Traffic, Residential, Commercial	Oct, 2015 – May, 2016			5.45 – 36.6	Ray et al., 2017
Uttar Pradesh	Agra	Oct, 2015 – Feb, 2016	Gas + TSP	16	624 in TSP 4015 in Gas	Verma et. al., 2017
	Agra	Oct, 2015 – Feb, 2016	Gas + TSP	2 Nitro PAHs	33.7 ± 2.9 in TSP 17.8 ± 6.1 in Gas	
	Urban, Traffic, Residential, Commercial	2010	PM_{10}, $PM_{2.5}$	13	845-1636 205-767	Singh et al., 2012
	Industrial	May, 2006 – Dec, 2009	TSP	16	72.7	Lakhani, 2012
	Urban, Traffic, Residential, Commercial	2006	PM_{10}	16	97.9, 18.4	Masih et.al., 2010

Srinagar	Urban	2008-2009	TSP	13	171	Huma et al., 2016
Jalandhar	Urban	Apr, 2012 – Mar, 2013	TSP	16	77.04-81.6	Kumar et.al., 2014
Barapani	North East Himalaya, Remote Area	2010	$PM_{2.5}$	16	4 - 46	Rajput et al., 2013
Chennai	Urban	Mar, 2009 – Feb, 2010	$PM_{2.5}$	11	325.7 to 790.8	Mohanraj et.al., 2011a
Tiruchirappalli	Urban, Traffic, commercial	2009-2010	$PM_{2.5}$	-	333.7	Mohanraj et.al., 2011b
Lucknow	Bhithauli Rural	27, June – 5, July 2006.	$PM_{2.5}$, PM_{10}	7	6.21 ± 1.54 to 12.43 ± 1.15 in $PM_{2.5}$ and 7.75 ± 1.42 to 15.77 ± 1.05 in PM_{10}	Ansari et al., 2010

3. OBJECTIVES

The literature review clearly suggests that the studies conducted nationally focused primarily on determining the concentration of 16 priority PAHs at various locations and States, while very few studies focused on derivatives of PAHs i.e., NPAHs in the particulate phase. Despite its higher carcinogenic potential, no studies have been conducted in India to estimate the concentration in gas and particulate phase of derivatives of PAHs (NPAHs, OPAHs), and their impacts on human health. Hence, this study is planned with the following objectives:

1. To determine the concentrations of Oxy-PAHs, Nitro-PAHs and PAHs in the gas and particulate phase at two sites, Dayalbagh and Sikandra at Agra as well as the concentrations of OC and EC in the particulate phase and their ratios (OC/EC).
2. To study the spatial and seasonal variation of Oxy-PAHs, Nitro-PAHs and PAHs.
3. To determine the origins of Oxy-PAHs, Nitro-PAHs.
4. To assess the potential health risks to the inhabitants from derivatives of PAHs and parent PAHs present in the particulate and gas phase.

4. PROPOSED METHODOLOGY

Sampling Sites

Agra is a major urban population centre with relatively high emissions of particulate matter from a variety of sources including mobile sources, biomass burning, etc. and secondary aerosol formation, making it a suitable location to study particle toxicity. Sampling will be conducted at two sites simultaneously Sikandra a site influenced by anthropogenic activities and Dayalbagh with minimum anthropogenic activities.

Sample Collection

Aerosol samples will be collected at two locations in Agra, a traffic-dominated site (Sikandra on the rooftop of single-storeyed building) and Dayalbagh. At Dayalbagh the sampling will be carried out on the rooftop of the Science Faculty building, Dayalbagh Educational Institute. A High-Volume Air Sampler Model TE-1000X (TISCH International, USA) will be used to collect samples at both sites simultaneously. Samples will be collected on quartz fiber filter (QFFs) paper (10.16 cm in diameter) and polyurethane foam (PUF) plugs (8 cm long and 6 cm in diameter) for the particle phase and gas phase, respectively, at a constant flow rate (0.2 m^3min^{-1}). The sampling will be performed for 24 hours, and eight or four samples will be collected monthly (2/1 in a week) at each site. Before sampling, QFFs will be stored at 750 °C overnight in a muffle furnace to remove any sort of background contamination and will be sealed in aluminium foil packaging until use. Before and after sample collection, filter papers will be desiccated at room temperature for 24 hours and weighed using a microbalance (Mettler AJ 150). The difference in pre- and post-sampling weight will be calculated to determine the mass concentration of TSP. PUFs will be pre-cleaned in dichloromethane (DCM using Soxhlet extraction) prior to sampling. Cleaned PUFs will be wrapped in aluminium foil and baked in an oven at 70 ºC for 40 minutes to remove excessive DCM and transported to the field in zip-locked bags without being exposed to ambient air. After sampling QFFs and PUFs will be kept at -20ºC until extraction.

Sample Extraction and Clean up

QFFs will be cut into pieces and extracted at room temperature by ultrasonication in a mixture of Dichloromethane (DCM) and n-hexane (4:1 ratio), while the PUFs are Soxhlet extracted in DCM and n-hexane mixture. The organic extract for the particulate phase (QFFs extract) will be filtered through Sartorius (393) filter papers. The gas and particle phase extracts will be cleaned using a silica gel column, concentrated to 1.5 mL using rotavapor (BUCHI), and stored at -20^{O}C in glass vials until analysis.

Analysis of PAHs and its Derivatives

PAHs and their derivative compounds will be analyzed using Gas Chromatograph-Mass Spectrometer (GC-MS) following temperature gradient protocol as mentioned in Verma et.al., 2017. Helium will be used as a carrier gas. The mass scanning ranged between 50 to 500 m/z.

Monitoring of Ozone, NOx and Meteorological Parameters

Ozone and NOx and the meteorological parameters like temperature, solar intensity, Relative humidity, wind speed and wind direction will be measured using Weather station.

OC-EC Analysis

OC and EC concentration will be analyzed in particulate phase samples using a thermal gravimetric analyzer (Model 4000 Perkin Elmer). During TGA, sample materials will be evaluated for mass change as a function of temperature in an inert or oxidizing environment. The mass shift in an inert environment will be suggestive of OC, whereas the loss in an oxidizing environment will be indicative of EC.

Oxidative Potential and Health Risk Assessment

Cancer risk posed by derivatives of PAHs can be evaluated using toxic equivalent factors (TEFs). BaP is used as a reference for other PAHs due to its high carcinogenic potency, and TEF values are assigned to each PAH derivatives relative to BaP. The total PAH toxic potency is equivalent to the BaP equivalent concentration (BaP_{equiv}) will be calculated using eq 1:

$$BaP_{equiv} = C \times TEF \qquad (1)$$

where C is the amount of PAH (μg kg^{-1}) detected in the mixture and TEF is the toxic equivalent factor of each PAH derivative. Incremental Lifetime Cancer Risk (ILCR) through ingestion, inhalation, and dermal exposure will be calculated using the following equations:

$$\mathrm{ILCR}_{ing} = \frac{\mathrm{BaP}_{equiv} \times \left(\mathrm{CSF}_{ing} \times \sqrt[3]{\left(\frac{BW}{70}\right)} \right) \times IR_{ing} \times EF \times ED}{BW \times AT \times 10^{6}} \quad (2)$$

$$\mathrm{ILCR}_{inh} = \frac{\mathrm{BaP}_{equiv} \times \left(\mathrm{CSF}_{inh} \times \sqrt[3]{\left(\frac{BW}{70}\right)} \right) \times IR_{inh} \times EF \times ED}{BW \times AT \times PEF} \quad (3)$$

$$\mathrm{ILCR}_{dermal} = \frac{\mathrm{BaP}_{equiv} \times \left(\mathrm{CSF}_{dermal} \times \sqrt[3]{\left(\frac{BW}{70}\right)} \right) \times SA \times AF \times ABS \times EF \times ED}{BW \times AT \times 10^{6}} \quad (4)$$

where BaP_{equiv} is the total PAHs toxicity potential calculated using the toxic equivalency factor (TEF). The Oxidative Potential of derivatives of PAHs will be determined in particulate phase of the samples. For the current investigation, the oxidative potential will be assessed using the DTT assay (Cho et al., 2005).

Data Interpretation and Computation

The data generated will be computed by using statistical methods such as multivariate linear regression, t-test, correlation analysis. SigmaPlot 13.0, Origin Pro version 9.9, RStudio and Microsoft Excel 2010, SPSS version 16.0 will be used for data processing and statistical analysis.

5. EXPECTED OUTCOMES

Fine particulate matter (PM) in the atmosphere has been linked to a variety of health issues, including cancer, allergies, asthma, inflammatory reactions in the brain comparable to Alzheimer's disease, respiratory and cardiovascular illness (from chronic exposures), and mortality (following short term exposures in sensitive subjects). Chemical composition, size, and solubility are likely variables influencing PM toxicity, although specific causal links

between recorded effects and the proportion of PM responsible are currently under investigation. Through inhalation, PAH, NPAH and OPAH adsorbed on respirable particulate matter cause cancer. The findings of this study will thus;

- Distinguish between direct and secondary sources and also provide information on moveable and stationary sources of pollution of these organic chemicals in atmosphere.
- Aid in creation of effective strategies to mitigate the negative consequences of air pollution by determining the amounts to which an individual is exposed at various locations.
- Prompt change in combustion engine design to decrease NO_x emissions and encourage full combustion to reduce PAH and PAH emissions.
- Bring out important implications in various fields of research such as atmospheric chemistry, medicine, epidemiology, toxicology, and agriculture. The results of this study can also be utilized by agencies like:

  (a) Pollution Control Boards

  (b) Indian Council of Medical Research

  (c) Industrial Facilities and Automobile Industries

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